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AN INVESTIGATION OF THE INTERFACIAL POLYMERIZATION OF POLYAMIDES IN A TUBULAR REACTOR

A THESIS

Presented to

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by

William Wills Dowdy

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AN INVESTIGATION OF THE INTERFACIAL POLYMERIZATION OF POLYAMIDES IN A TUBULAR REACTOR

Approved:

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT	ii
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS	v
SUMMARY	vi
CHAPTER	
I. INTRODUCTION	1
II. THEORY	4
III. EQUIPMENT AND PROCEDURE	13
IV. DISCUSSION OF RESULTS	22
V. CONCLUSIONS	39
APPENDICES	40
BIBLIOGRAPHY	50

LIST OF TABLES

Table		Page
1.	Data Summary	45
2.	Reproducibility of Runs	49

LIST OF ILLUSTRATIONS

Figure		Page
1.	Schematic Diagram of Experimental Equipment	15
2.	Rotameter Calibration	17
3.	Productivity Ratio vs. (Sebacoyl Chloride) (HMDA) for 36.5 inch Reactor	24
4.	Productivity Ratio vs. $(\text{Sebacoyl Chloride})^{1.3}$ (HMDA) for 36.5 inch Reactor	25
5.	Productivity Ratio vs. (Sebacoyl Chloride) (HMDA) for 8.5 inch Reactor	26
6.	Productivity Ratio vs. $(\text{Sebacoyl Chloride})^{1.3}$ (HMDA) for 8.5 inch Reactor	27
7.	Productivity Ratio vs. $(\text{Sebacoyl Chloride})^{2}$ (HMDA) for 8.5 inch Reactor	28
8.	Productivity Ratio vs. (Sebacoyl Chloride) $(\text{HMDA})^{2}$ for 8.5 inch Reactor	29
9.	Comparison of Productivity Ratios of 8.5 inch and 36.5 inch Reactors	34

SUMMARY

The objective of this investigation was to study the key variables that affect interfacial polycondensation in a tubular reactor. The particular reaction studied was that of sebacoyl chloride and hexamethylene diamine to produce 610 Nylon (polyhexamethylene sebacamide). An insight into the nature of the reaction mechanism under these conditions was obtained from this study.

An attempt was made to measure absolute reaction rates of this extremely fast reaction; however, this effort was not too fruitful as it was impossible, in many cases, to stop the reaction before formation of polymer film reduced the reaction rate. However, in runs at low concentrations where film formation was not a factor, it was found that interfacial polycondensation proceeded at essentially the same rate as the reaction between aliphatic acid chlorides and primary amines.

The tubular reactor was constructed of 3/8 inch outside diameter stainless steel tubing having an inside diameter of 0.305 inches. Reactor lengths of $8\frac{1}{2}$ and $36\frac{1}{2}$ inches were used. All reactions were conducted at atmospheric pressure and a temperature of 68.0° F. Runs were conducted at Reynolds numbers of 17,050, 24,200, 33,850, and 40,500. Productivity ratio, defined as grams of sebacoyl chloride

consumed per kilogram of reactor effluent, was determined by quenching a sample of reactor effluent in acid solution and measuring the amount of polymer contained in the sample.

Reynolds number, concentration of reactants, and degree of dispersion of organic phase were found to be the key variables that affect productivity ratio, yield, and per cent conversion of the reactants. Reaction time is unimportant as the reaction is completed in a fraction of a second. The reaction rate was found to be second order with respect to reactant concentrations.

It was concluded that extremely high shear is needed to disrupt the polymer film formed at the interface in order that the reaction may proceed nearly to completion. For this reason, a tubular reactor probably would not be used for commercial production of a polymer or copolymer by interfacial polycondensation. A reactor equipped with a high shear rotor, such as a flat or perforated disc, would be needed.

For future work, it is recommended that means of obtaining better dispersion of the organic phase be investigated. A transparent reactor and high speed photography could be used to determine droplet size and thereby study the effect of interfacial area.

CHAPTER I

INTRODUCTION

For many years condensation polymerizations have been based on slow, reversible organic reactions. These reactions are usually carried out in the melt and employ a reduced pressure cycle to facilitate the removal of volatile by-products. Melt condensations are complicated, require expensive equipment, and are difficult and time consuming to reproduce in the laboratory. Since melt polycondensations are usually carried out at temperatures between 200 and 300° C., the method is limited to polymers and intermediates that are stable at these temperatures.

In the past few years, considerable interest has been aroused in interfacial polycondensation as high polymers can be produced rapidly in inexpensive equipment under atmospheric conditions by this method. Interfacial polymerization is based on the Schotten-Baumann reaction of an acid halide with a compound containing an active hydrogen atom. In this process the irreversible polymerization of two fast-reacting intermediates occurs at or near the interface of a heterogeneous liquid stystem.

Thus far interfacial polycondensation has been employed chiefly as a laboratory technique for preparing conventional as well as new

and novel polymers and copolymers. With a minimum of time and equipment, the polymer chemist can now prepare and evaluate many polymers which were not previously accessible by the melt method. Most of the typical condensation polymers, such as polyamides, polyesters, polyurethanes, polyureas, polysulfonamides, etc., have been prepared by this method.

No polymers or copolymers are known to be produced commercially by this process although it could readily be scaled up or made continuous. The use of large amounts of solvents, the formation of a fair amount of salt, and the expense of diacid halides are the chief drawbacks to commercialization. It is anticipated, however, that someday novel polymers may be discovered that can be produced only by this technique, and this would necessitate commercialization of this polymerization process. The anticipated eventual commercial use of interfacial polymerization inspired the selection of this polymerization process as the subject of this study.

Previous studies of this polymerization reaction have been limited to continuous removal of a polymer film formed at the interface of two stagnant liquid layers or to preparations in Waring blenders (1, 7). Both of these methods have serious drawbacks for studying extremely fast reactions and determination of exact reaction rates. In this study the deficiencies associated with the other techniques were minimized by carrying out the reactions in a tubular reactor attached to a mixing tee.

The interfacial polycondensation of 610 Nylon (polyhexamethylene Sebacamide) was selected as the specific reaction for study. The formation of 610 Nylon was accomplished by reacting sebacoyl chloride dissolved in carbon tetrachloride with hexamethylene diamine (HMDA) dissolved in water. Sodium hydroxide was also dissolved in the aqueous phase to neutralize the hydrochloric acid generated by the reaction.

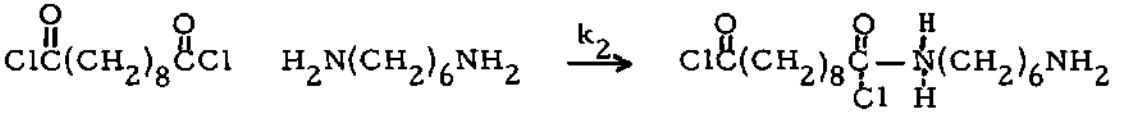
The effect of the following variables on reaction rate were evaluated: (a) reactant concentrations, (b) Reynolds number, (c) addition of detergents, (d) reactor length, (e) degree of dispersion of the organic phase, and (f) ratio of reactants.

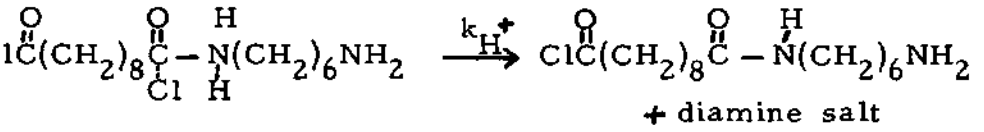
The data collected in this investigation cannot be compared with any other, as no data on interfacial polycondensations in tubular reactors have been reported in the literature.

CHAPTER II

THEORY

The chemistry of interfacial polycondensation has been described by Morgan and Kwolek (2), and their explanation will be restated here. The reaction between a diacid chloride and a diamine will be used as a typical example. The reaction proceeds in the following manner:





$$k_H^+ > k_2 > \text{"}k_{\text{reactant mixing}}\text{"}$$

Intermediates of this type are believed to react by an S_N2 (nucleophilic) mechanism to form a protonated amide from which a proton is rapidly eliminated in the presence of more base. The proton acceptor is presumably an amine group on a diamine molecule or the end of an oligomer chain. Water also could act as the proton carrier. The amine can be regenerated in the aqueous phase by the use of inorganic base.

High polymer forms in a fraction of a second when a diacid chloride solution is brought into contact with an aqueous diamine solution. In this period of time, equivalents of the reactants must combine nearly quantitatively, eliminate two equivalents of hydrogen chloride, and form a precipitate. In order to achieve this, the reaction rates must be extremely fast, and indeed the absolute reaction rates of unhindered aliphatic acid chlorides with primary diamines have so far been immeasurably fast but have been estimated to be between 10^2 to 10^4 liters/mole-second in homogeneous solution (2). The criterion for high polymer formation is that the reaction rate must be faster than mixing and considerably faster than any important side reaction at the polymerization site. Also, there must be sufficient time to essentially complete the polymerization before the polymer precipitates or gels.

In an unstirred system direct and indirect evidence points to the formation of most condensation polymers in the organic phase. The primary functions of the aqueous phase are to serve as solvent medium for the diamine and the acid acceptor and to remove by-product acid from the polymerization zone. The interface provides through solubility differences a controlled introduction of the aqueous reactant into an excess of diacid halide in the organic phase adjacent to the interface.

Upon phase contact both reactants and solvents tend to become

partitioned with the opposite phase. The diamine nearly always has an appreciable potential partition toward the organic phase, whereas the acid chloride has very little solubility in water. Measured equilibrium partition coefficients ($C_{H_2O}/C_{Solvent}$) for diamines in useful solvent systems have varied from 400 to less than 1 (4). The values are used to estimate the relative tendency of diamines to transfer to the organic phase during polymerication. Partition equilibria are never achieved during polymerization, because acylation takes place in the organic phase as rapidly as diamine is transferred; therefore, the mass transfer of diamine is the rate-controlling step at all concentrations.

During polycondensation the first diamine meets a high concentration of acid chloride and is acylated to a large extent at both ends. The following diamine finds a layer of acid chloride-terminated oligomers plus diacid chloride. The reaction proceeds by an irreversible coupling of the oligomers by the diamine. The concentration and size of oligomers increases until a layer of high polymer is obtained. Thus, high polymer forms because of the high reaction rate and the increasing probability that diamine reacts with an oligomer rather than new diacid chloride.

During this period of rapid reaction, there is presumably some diffusion of oligomers further into the organic phase, but the diffusion of polymer chains is relatively slow. There is also an

entry into the reaction zone of diacid chloride by diffusion. Since the reaction is appreciably exothermic, local movement may be increased by the heat imparted to the reactants and solvents. Much of this energy presumably is absorbed by the solvents.

It may be considered that the reaction takes place in a series of incremental layers through which the diamine advances from the interface; the reaction rate exceeds diamine flow. An initial layer of polymer forms as the amount of diamine becomes equal to the acid chloride. The polymer in this layer becomes capped with amine groups and diamine passes on to the next layer. In successive layers the acid chloride concentration is initially higher than that of diamine. Simultaneously the diamine flow drops off because of the recession of the reaction zone into the organic phase and the increased resistance to diffusion brought about by formation of polymer gel. There may exist in the final film a gradation of average molecular weights and ratio of end groups from one face of the film to the other.

Following the initial fast addition of diamine to acid chloride, hydrogen chloride is eliminated in a still faster step and transferred to the aqueous phase. Elimination and transfer of the hydrogen and chloride ions are presumed to occur with the assistance of water or amine. Hydrogen chloride is retained in the aqueous phase as the diamine salt or it may be neutralized there by an inorganic base.

Experiments have shown that acid chloride hydrolysis takes place exclusively in the aqueous phase (4). Most diacid chlorides have low solubility in water and thus are protected from hydrolysis. The shorter chain aliphatic acid chlorides are the most water soluble and consequently are hydrolyzed to the greater extent.

As the concentration of polymer species increases, interchain contacts increase until a compact network is formed and precipitation results. At the point where a coherent film is formed, polymerization does not stop entirely but is greatly decreased in rate because of the lower mobility of the polymer chains and the decreased diffusion rate of the reactants. While the initial polymer reaches the maximum molecular weight permitted by the system, there is a secondary growth of low polymer in the spaces of the gel and upon the face of the film touching the organic phase. This leads to a lowering of the average molecular weight and a broadening of the molecular weight distribution.

The mechanism for stirred polymerization is the same as for unstirred except that stirring assists the transfer of reactants and by-products. When thin films form about the droplets of reactant solution, they may be torn away and fresh surface exposed for renewed reaction.

The question arises as to what differences, if any, exist between melt condensation polymers and polymers produced by inter-

facial polymerization. In general there are no differences between polymers produced by the two methods as interfacial polymers are usually normal, linear condensation polymers. The acid chloride end groups of interfacial polymers are hydrolyzed to yield stable carboxyl end groups.

610 Nylon produced in a Waring blender by Beaman, Morgan, et. al. (3) had an inherent viscosity of 2.06, a number average molecular weight of 18,900, thirty-seven equivalents of amine end groups, and sixty-nine equivalents of carboxyl end groups per million grams of polymer. These values are typical of those obtained for melt condensation polyamides. It is interesting to note that both melt and interfacial polyamides have a high ratio of carboxyl to amine end groups. In melt condensation, this arises from loss of diamine through vaporization during the condensation cycle. In interfacial polymerization this probably arises from a combination of acid chloride hydrolysis and capping of polymer ends by acid chloride.

Very few data have been reported on the subject of molecular weight distribution of interfacial polyamides, but Wittbecker and Morgan (1) report that in general the molecular weight distribution of interfacial polyamides is similar to or even narrower than those resulting from melt polymerization. The paucity of this information can be attributed to the fact that molecular weight fractionation of polymers is a tedious and time consuming operation.

Even though the polymers produced by the two condensation methods are essentially identical, vast differences exist in the basic polymerization principles of the two methods. Melt condensation stresses the principles of high purity of intermediates, exacting balance of reacting components, and high yield. In interfacial polycondensation, all three of these principles appear to have been violated.

It is not surprising that most impurities cannot be tolerated in a homogeneous melt polymerization with temperatures approaching 300° C. However, because of the mild reaction conditions of interfacial polycondensation, a greater number of the impurities frequently present in organic intermediates are unreactive. In other words, functional groups which are much less reactive than the two upon which the polycondensation is based can be present without interfering with the formation of polymer of high molecular weight. In addition, the heterogeneity of this polymerization keeps some of the impurities, especially those that are very soluble in water, from ever reaching the reaction zone. As is the case with melt polymerization, reactive monofunctional intermediates will limit the molecular weight by chain termination, and reactive intermediates with a functionality greater than two will branch and finally crosslink the polymer.

In a homogeneous, melt polycondensation the two different

functional groups must be present in equivalent amounts or the polymer chains stop growing when they are all terminated by the same group. A chemical balance is attained in polyamides by the use of a balanced diamine-dibasic acid salt. Since interfacial polycondensation is a heterogeneous reaction and the reactants must diffuse toward the interface, large excesses of one of the reactants can be tolerated without limiting the molecular weight. In other words, reactant equivalence is attained in the polymerization zone even though the system taken as a whole is unbalanced. Thus, two moles of diamine and one mole of diacid chloride will produce high molecular weight polymer, although the reactant stoichiometric ratio is one to one.

In melt polycondensation, it is necessary for a successful reaction to proceed very nearly to completion, without side reactions that consume the functional groups that are needed for the production of large, linear molecules. In contrast, it is not necessary for interfacial polycondensation to proceed quantitatively; high molecular weight polymers have been prepared in yields as low as 5 per cent.

It might be expected that interfacial polycondensation would fail to yield high polymers, since either hydrolysis of one end of diacid chloride just before the other end reacts with an amine group or hydrolysis of an acid chloride group on the end of a growing polymer chain would lead to early termination of the polymerization.

It must be concluded, however, that actually these side reactions are negligible, since high molecular weights are obtained from properly run interfacial polycondensations.

Since interfacial polycondensation is an irreversible random coupling of complementary components with the elimination of a by-produce, such as hydrogen chloride, there is no interchange between linkages once they are formed. Thus, a major difference between this polymerization and conventional melt polycondensation is that there is no equilibration among polymer species of varying molecular weights. The distribution of chain lengths resulting from melt polycondensation is known from theoretical considerations (8) and actual fractionation data (9). Interfacial polycondensation, however, leads to various distributions, depending on reaction conditions.

CHAPTER III

EQUIPMENT AND PROCEDURE

The items of equipment used in the experimental work were two ten-gallon, stainless steel tanks; several 1/4 inch stainless steel globe valves; two thermometers; three stainless steel centrifugal pumps manufactured by Eastern Industries, Inc.; two heat exchangers which consisted of loops of stainless steel tubing submerged in buckets of ice water; two Fisher and Porter rotameters; a glass acid reservoir; a standard 1/4 inch stainless steel pipe tee which served as a mixing tee; a tubular reactor constructed of various lengths of 3/8 inch stainless steel tubing; a quick opening valve; and a drying oven. A schematic diagram of the experimental equipment is shown in Figure 1.

In order to minimize corrosion and prevent contamination of the solutions, all equipment and piping which contacted the sebacoyl chloride, hydrochloric acid, and hexamethylene diamine solutions were constructed of either stainless steel, glass, or polyvinyl chloride plastic.

In order to prevent reaction of the solutions with gases in the air, the sebacoyl chloride holding tank was vented to the atmosphere through a water absorption train consisting of drierite, calcium

chloride, and a bubbler of sebacoyl chloride solution. Similarly, the diamine tank was vented to a carbon dioxide absorption train consisting of calcium oxide and a bubbler of hexamethylene diamine solution.

A HMDA stock solution of ca. 0.5 molar was made up when needed by adding 1-2 liters of 85 per cent Nylon grade hexamethylene diamine (supplied by the Du Pont Company) and 10-15 liters of distilled water to a 5-gallon, glass carboy. Ten ml. of the resulting solution were titrated with standardized HCl solution to the methyl red endpoint to determine the molarity of the HMDA solution. Since the volume of water and concentrated HMDA added to the carboy were accurately known, the number of moles of HMDA in the carboy could be calculated. Two moles of sodium hydroxide for each mole of HMDA in the carboy were added to ca. two liters of distilled water, and the volume of the sodium hydroxide solution at room temperature was noted. The sodium hydroxide solution was then added to the carboy, and the HMDA molarity was recalculated to correct for dilution. Calculated amounts of HMDA stock solution and water were then added to the HMDA solution holding tank.

Sebacoyl chloride solution of the desired molarity was obtained by adding a measured amount of pure sebacoyl chloride (obtained from Trubeck Laboratories) to a measured volume of carbon tetrachloride. The sebacoyl chloride was measured in graduated pipettes,

Key: 1,2 Stainless Steel Tanks; 3, 4, 5, 6, 7, 8 Globe Valves; 9, 10 Thermometers; 11, 12, 13 Centrifugal Pumps; 14, 15 Heat Exchangers; 16, 17 Rotameters; 18 Acid Reservoir; 19 Mixing Tee; 20 Quick Opening Valve; 21 Tubular Reactor

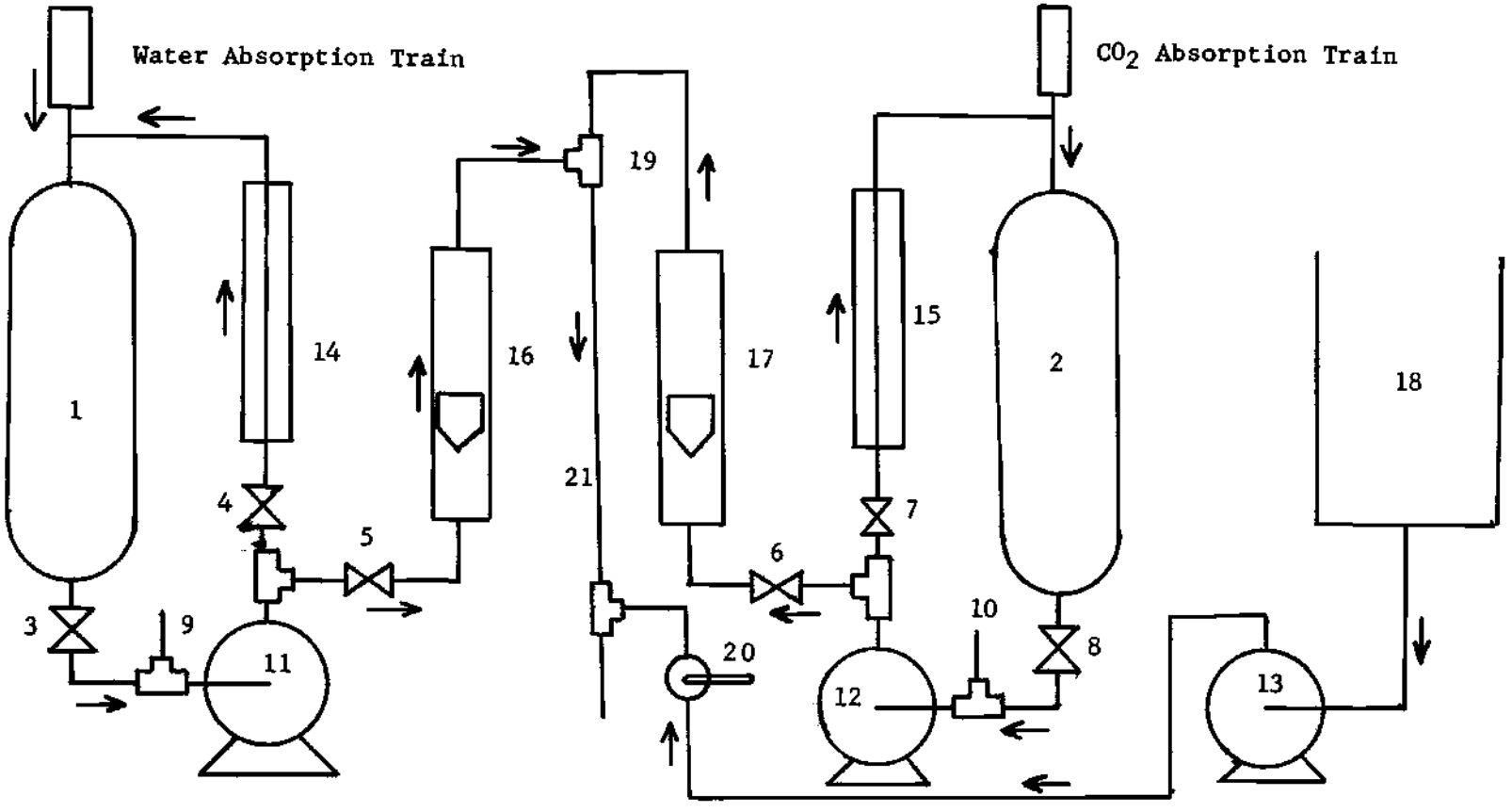


Figure 1. Schematic Diagram of Experimental Equipment

and the carbon tetrachloride was measured by weighing. The resulting solution was then added to the sebacoyl chloride solution holding tank.

All runs were made at a temperature of 68.0° F. This temperature was chosen because ambient temperature was always somewhat higher than this; therefore, this temperature could always be readily obtained by cooling of the solutions. Cooling of the solutions was accomplished by recirculating the contents of the tanks through a heat exchanger. The heat exchanger consisted merely of a coil of stainless steel tubing immersed in a bucket of ice water. Solution temperatures were measured by thermometers located on the suction side of each centrifugal pump. The recirculating flow rate was controlled by adjusting a metering valve so that both solutions reached a temperature of 68.0° F. simultaneously.

When both solutions reached a temperature of 68.0° F., recirculation was stopped and the flow was diverted through the rotameters. The rotameters had a nominal capacity of two gallons of water per minute, but this could be increased by changing floats. The rotameters were calibrated for both water and carbon tetrachloride (see Figure 2). The flows to the rotameters were adjusted by manipulation of metering valves until the desired flow rates were obtained. The aqueous stream entered the back connection of the 1/4 inch pipe mixing tee, and the organic stream entered the side

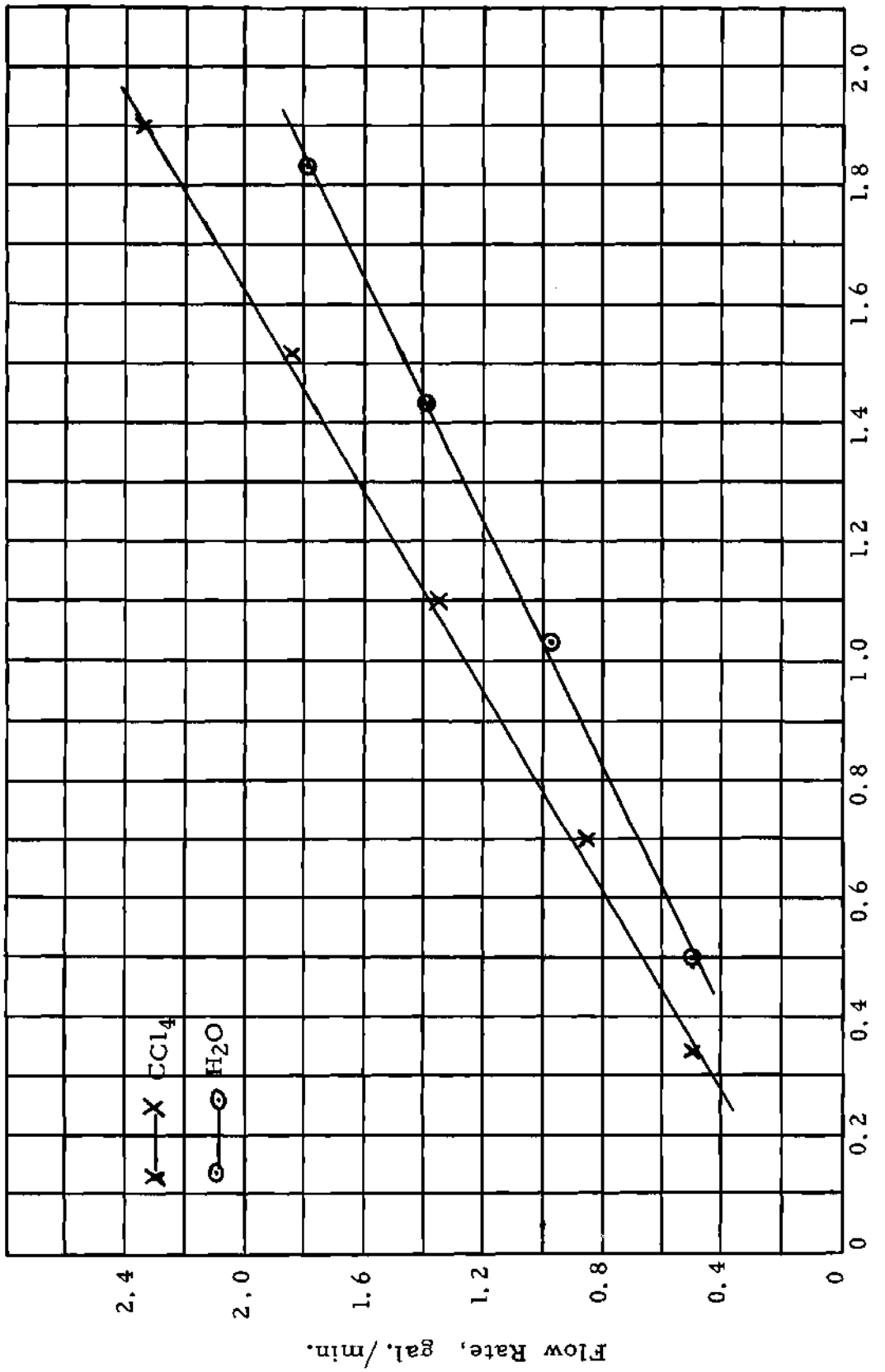


Figure 2. Rotameter Calibration

connection of the tee. After merging in the mixing tee, the streams entered a tubular reactor which consisted of either an $8\frac{1}{2}$ inch length or a $36\frac{1}{2}$ inch length of 3/8 inch OD -0.305 inch ID stainless steel tubing.

When the flows through the rotameters had settled down to the desired rates, the reactor effluent was sampled by rapidly inserting a tared beaker containing ca. 1800 ml. of 2N HCl solution under the reactor exit. The contents of the beaker were vigorously stirred during and after the sampling period. The beaker was removed after ca. one liter of sample had been collected. The beaker was reweighed to determine the exact weight of sample collected. The acid in the beaker immediately neutralized the remaining HMDA and sodium hydroxide in the sample thereby terminating the reaction.

After 25 runs had been made, it was feared that the acid in the beaker might not be neutralizing the basic sample rapidly enough; therefore, a 1/4 inch pipe tee was connected to the reactor exit; and an acid injection system consisting of an acid reservoir, a centrifugal pump, and a quick opening valve was piped to the side connection of the tee.

The procedure for operating the acid injection system was the following. About a liter of 2N hydrochloric acid was poured into the acid reservoir; the pump was turned on and some acid was pumped through the valve to assure that the line to the valve was

full of acid. The valve was then closed, the pump turned off, and the reservoir removed after the flexible hose attached to it had been sealed off by pinchclamps. The reservoir was weighed and this weight recorded as the initial weight. The reservoir was then replaced in the system, the pinchclamps loosened, and the pump turned on with the discharge valve closed. When the flows of the two reactant streams through the reactor had become steady, the run was sampled in the normal manner except that the quick-opening valve was opened at the same instant the beaker was inserted under the reactor exit. At the termination of sampling, the valve was closed an instant before the sampling beaker was removed. The valve was positioned above the injection tee; consequently the line from the valve to the tee was empty prior to and at the end of each run. After each run the acid reservoir was removed and reweighed to determine the amount of acid that had been injected. The weight of acid injected varied between 125-300 grams per run, depending upon reactant flow rates. The weight of the beaker was determined and the weight of injected acid was subtracted from the gross weight of sample to yield the net weight of sample collected per run.

At the completion of the weighing operation, the sample was tested with indicator paper to make sure that it was acidic (all samples were acidic). Since 610 Nylon of all molecular weights is insoluble in both water and carbon tetrachloride (2), it was a simple

matter to separate the polymer gel from the liquid by filtration through a fritted glass funnel. The polymer was washed with water several times to remove salts and some of the organic solvent. The wet polymer gel was collected on a tared watch glass and placed in a 215-220° F. oven to drive off water and carbon tetrachloride. The sample was dried until a constant weight was obtained on a four place analytical balance.

The dry weight of polymer was multiplied by 0.846 to convert from weight of polymer to weight of sebacoyl chloride reacted to produce the polymer. The factor 0.846 is the ratio of the molecular weight of sebacoyl chloride to that of a repeat unit of 610 Nylon. The molecular weight of sebacoyl chloride is 239.0 grams, and the weight of a repeat unit of 610 Nylon is 282.4 grams. Since one mole of sebacoyl chloride and one mole of HMDA react to produce one repeat unit of polymer, the weight of polymer must be multiplied by 239.0/282.4 to calculate the amount of sebacoyl chloride consumed. The weight of the polymer end groups may be neglected in this calculation as the molecular weight of 610 Nylon produced by this method is high; the number average molecular weight equals 18,900 (3). The grams of sebacoyl chloride reacted per kilogram of reactor effluent sample collected were calculated. This quantity is an indication of the productivity of the overall process which includes both kinetic and diffusional mechanisms. It will be referred to as the producti-

vity ratio. Per cent conversion (yield) was also calculated. Per cent conversion indicates the weight of the reactant present in smaller amount reacted divided by the original weight of this component; the quotient was multiplied by 100 to convert to per cent.

Beaman, Morgan, et al. (3) suggested use of reactant concentrations such that only 1-3 grams of polymer are produced for every 100 ml. of combined water and organic solvent. In this work, only 1-3 grams of polymer were produced per kilogram of combined solvents. Low reactant concentrations were deliberately chosen to avoid possible plugging of the reactor and to minimize temperature rise at the interface due to heat generated by the reaction. It was necessary, however, to disassemble and clean the reactor and mixing tee after each run in order to get rid of polymer gel deposits.

CHAPTER IV

DISCUSSION OF RESULTS

Fifty-five experimental runs were made. The process conditions and results of these runs are summarized in Table 1, Appendix B.

Polymerization temperature for all the runs was held constant at 68.0° F. Reactor exit temperatures were measured at several conditions and found to be the same as the temperatures of the entering streams; therefore, the reactions were conducted at adiabatic, isothermal conditions. Sebacoyl chloride solutions with molarities over the range 0.0478 to 0.1913 and hexamethylene diamine solutions over the molarity range of 0.030 to 0.1518 were used. The molar ratio of HMDA to sebacoyl chloride in the reactor varied from 4:1 to 1:2. Reactor Reynolds numbers of 17,050, 24,200, 33,850, and 40,500 were used for the various runs. The method used to calculate the Reynolds numbers is shown in Appendix A. Acid injection into the reactor was used in the last thirty runs. Reactor lengths of $8\frac{1}{2}$ and $36\frac{1}{2}$ inches were used for the first twenty-five runs. The addition of the acid injection tee increased the reactor lengths by 5/8 - 3/4 inches. The reactor was constructed of standard 3/8 inch OD stainless steel tubing. In each run equal flow rates by

weight of the two reactant streams were maintained.

Productivity ratios, reported as grams of sebacoyl chloride consumed per kilogram of reactor effluent sample, are plotted in Figures 3 - 8 as a function of reactant concentrations and Reynolds numbers. Some of the figures feature reactant concentrations raised to powers other than unity. This was done to assess fully the effect of reactant concentrations on productivity ratio; this will be discussed later in more detail. The data for the two reactor lengths are plotted separately, although it is seen that reactor length does not have an appreciable effect on productivity ratio.

The term "productivity ratio" was coined to describe the overall reaction process. The reaction process is affected by the absolute reaction rate of the polymerization reaction; the diffusion of reactants, products, and by-products; and Reynolds number. Productivity ratio is defined as the weight in grams of the reactant present in smaller concentration reacted per kilogram of reactor effluent. In most of the runs, sebacoyl chloride was the reactant present in lower concentration. In the runs where hexamethylene diamine was present in lower concentration, the moles of HMDA reacted were converted to moles of sebacoyl chloride and subsequently to grams of sebacoyl chloride and reported as such. Productivity ratio is reported as grams of sebacoyl chloride reacted per kilogram of sample for all the experimental runs. It is seen that

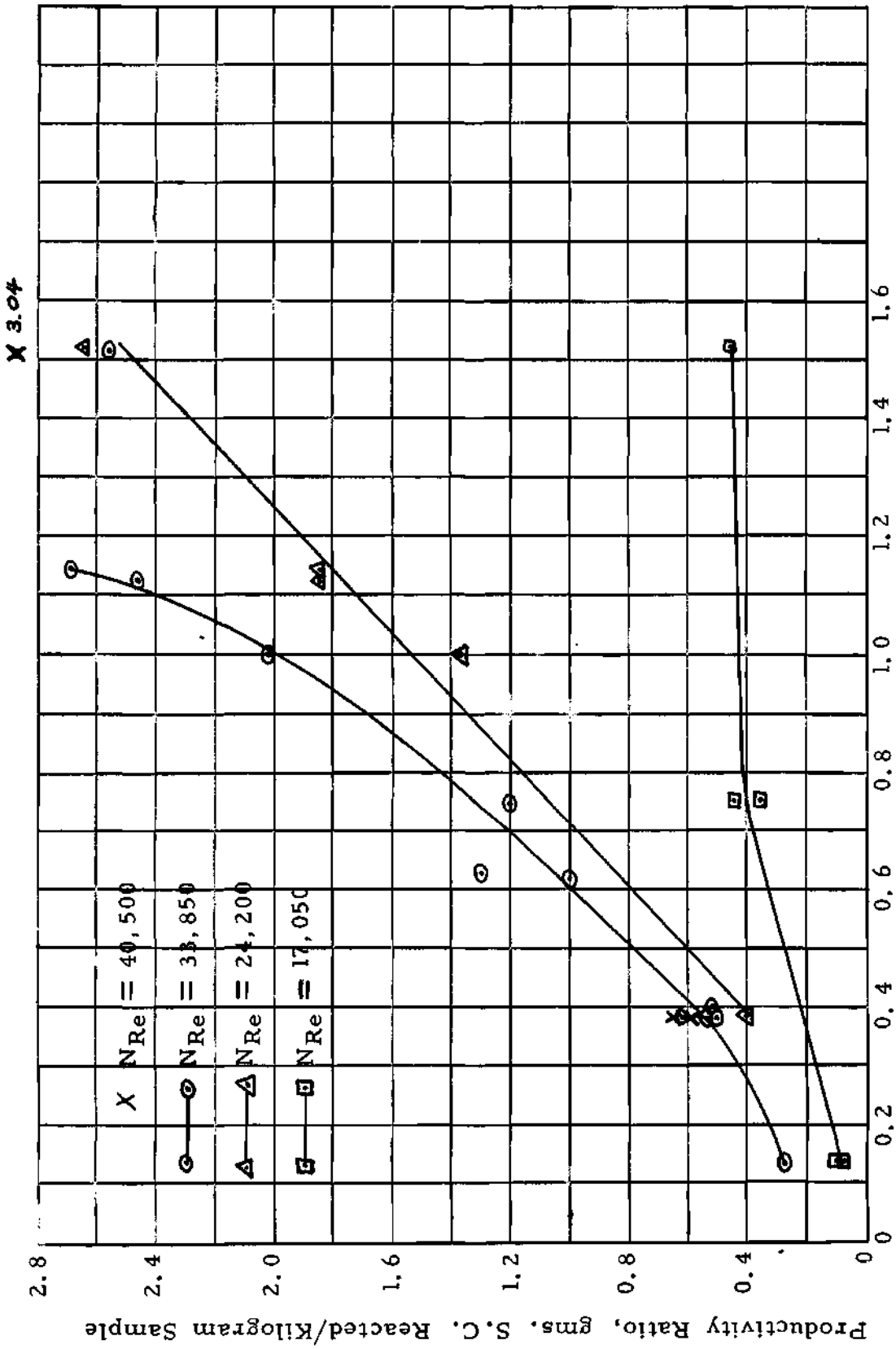


Figure 3. Productivity Ratio vs. (Sebacoyl Chloride)(HMDA) for 36.5 inch Reactor

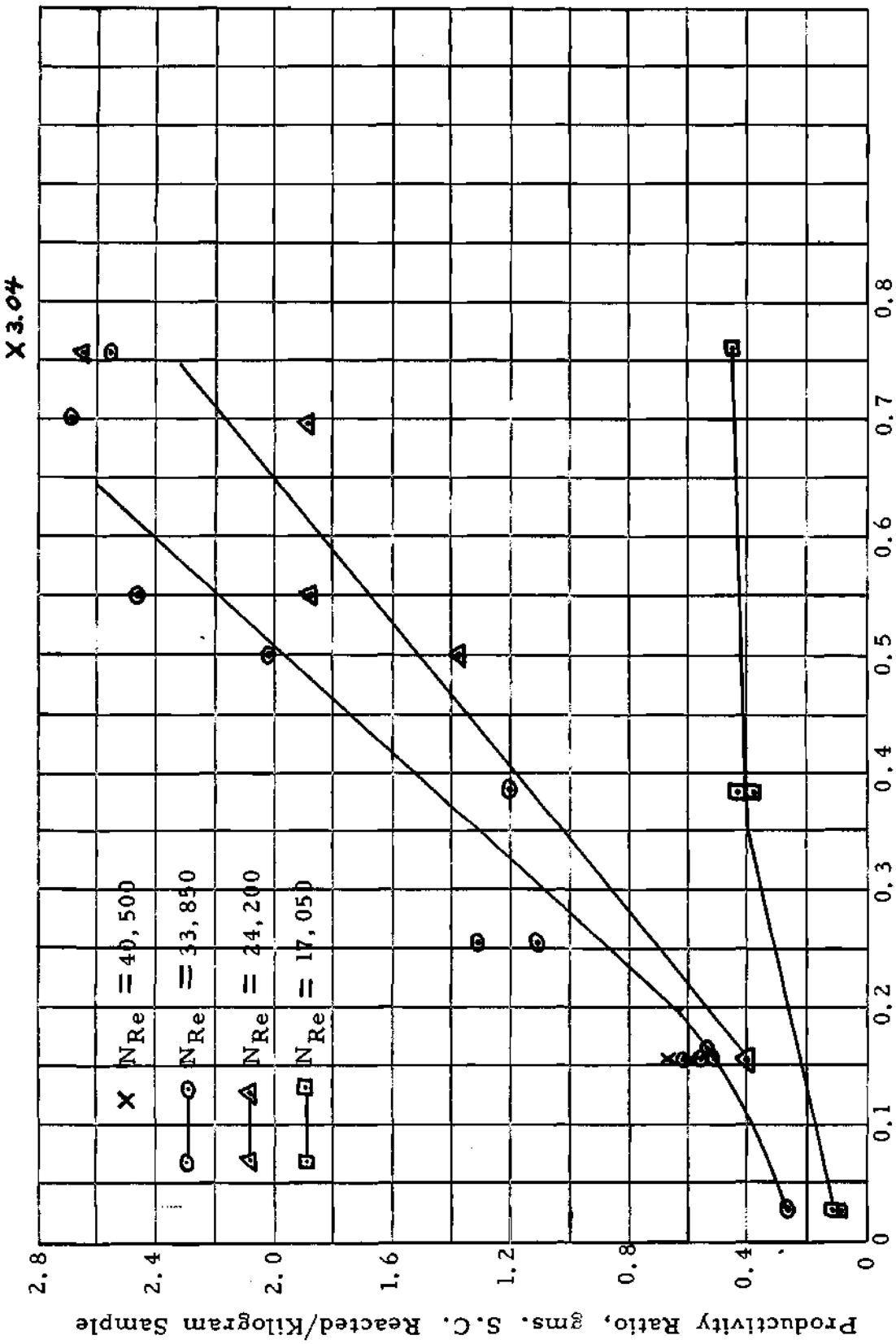


Figure 4. Productivity Ratio vs. (Sebacoyl Chloride)(HMDA) for 36.5 inch Reactor

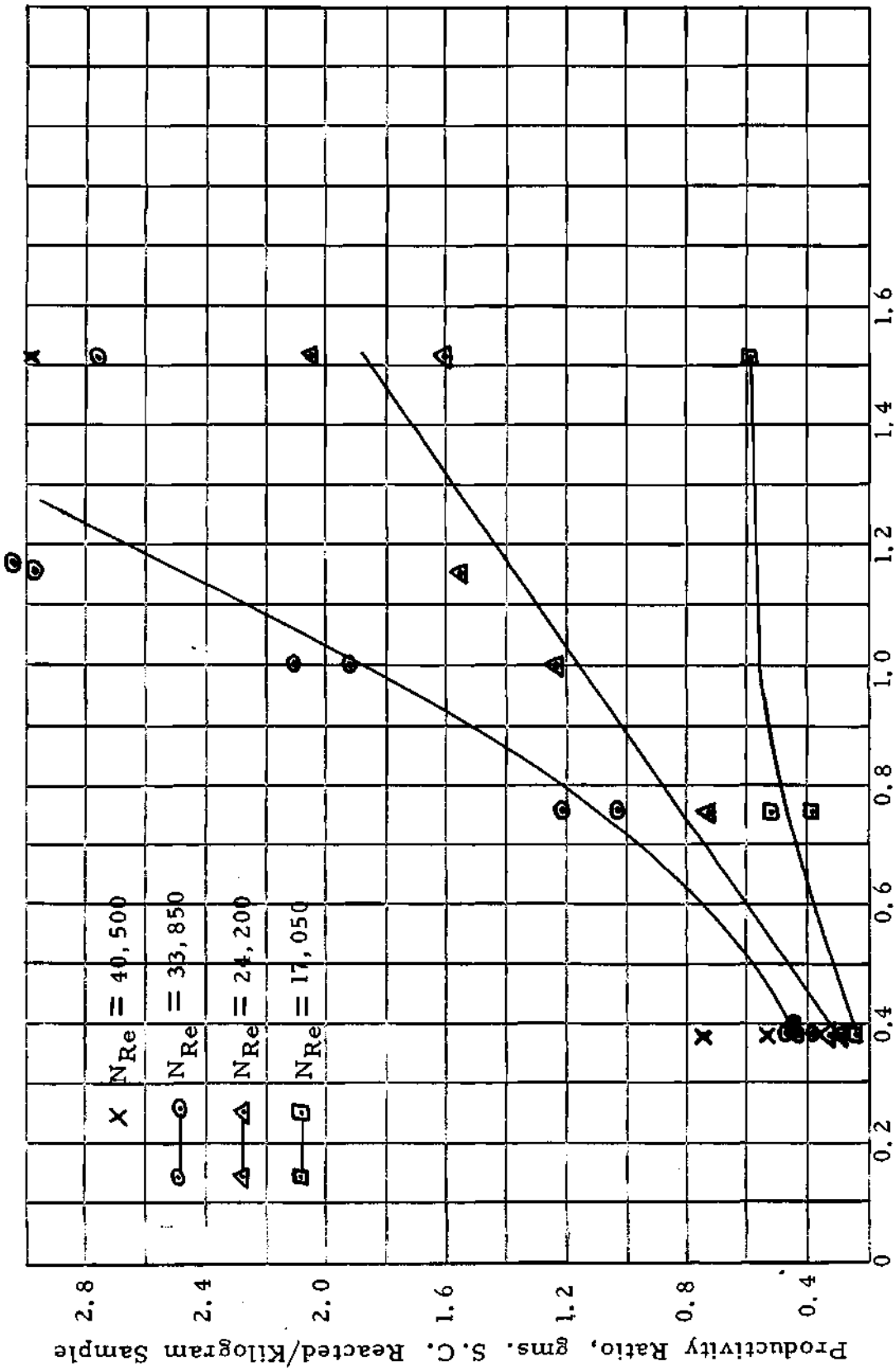


Figure 5. Productivity Ratio vs. (Sebacoyl Chloride)(HMDA) for 8.5 inch Reactor

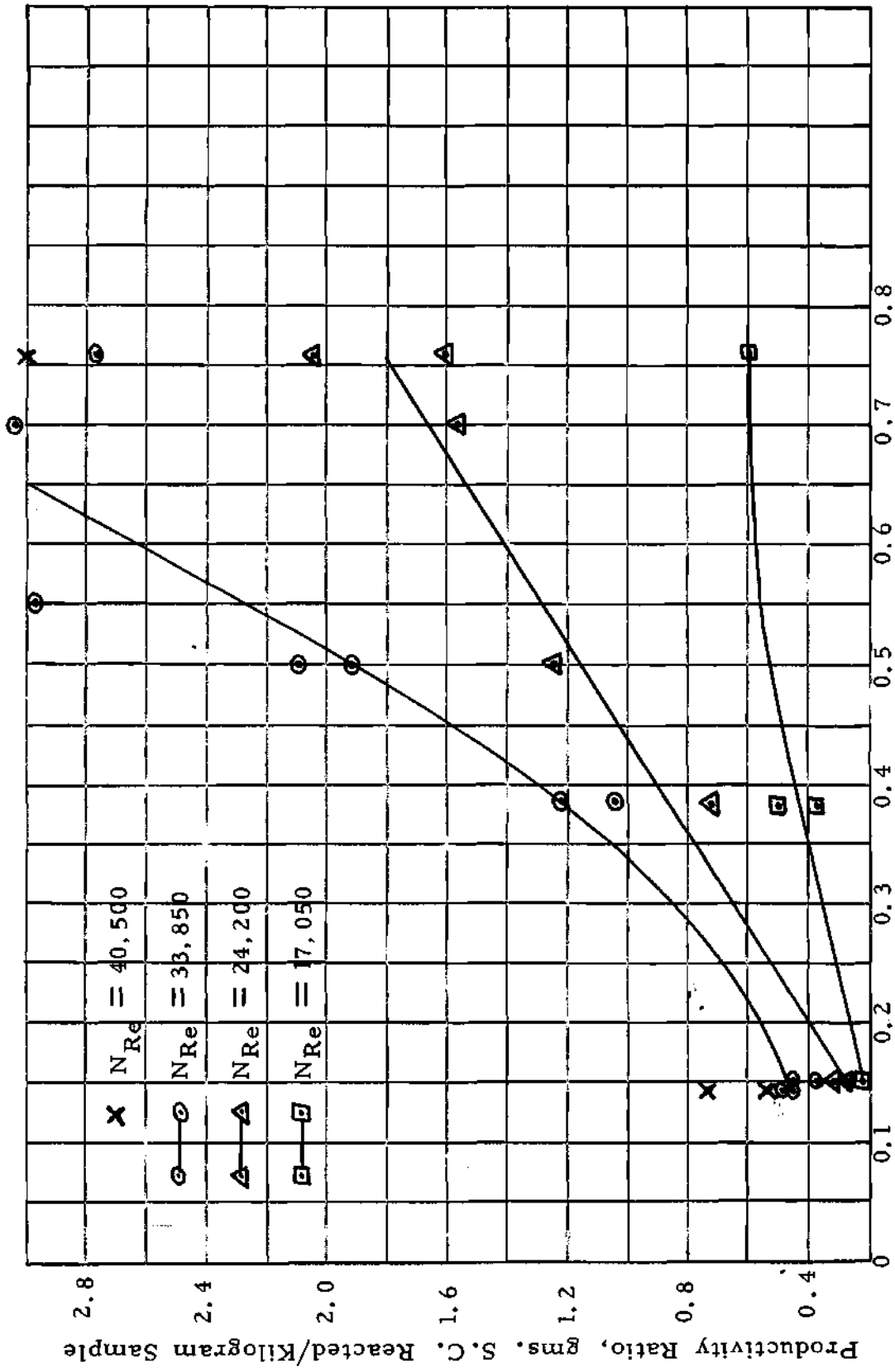


Figure 6. Productivity Ratio vs. (Sebacoyl Chloride)^{1,3}(HMDA) for 8.5 inch Reactor

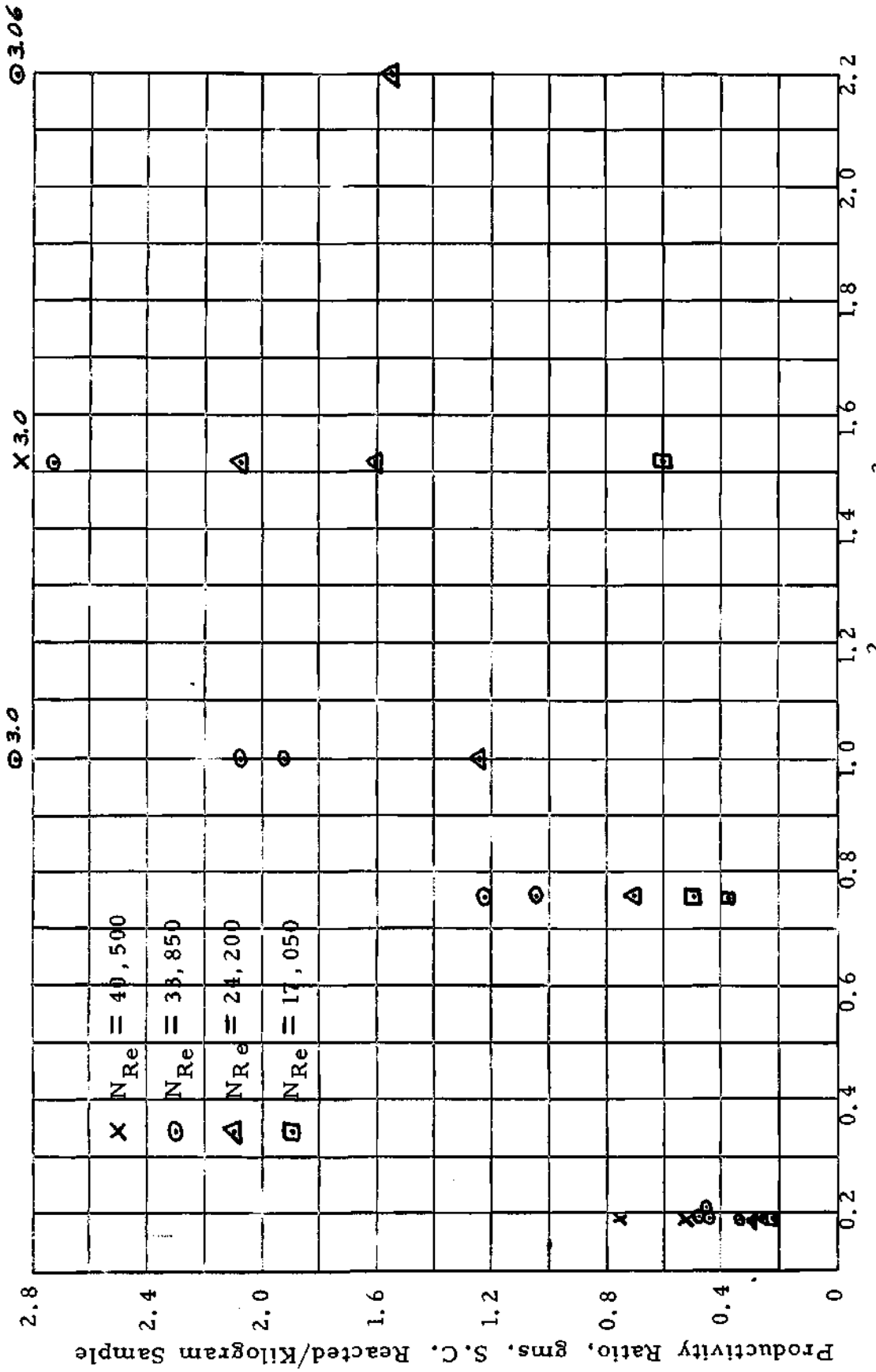


Figure 7. Productivity Ratio vs. (Sebacoyl Chloride)(HMDA) for 8.5 inch Reactor

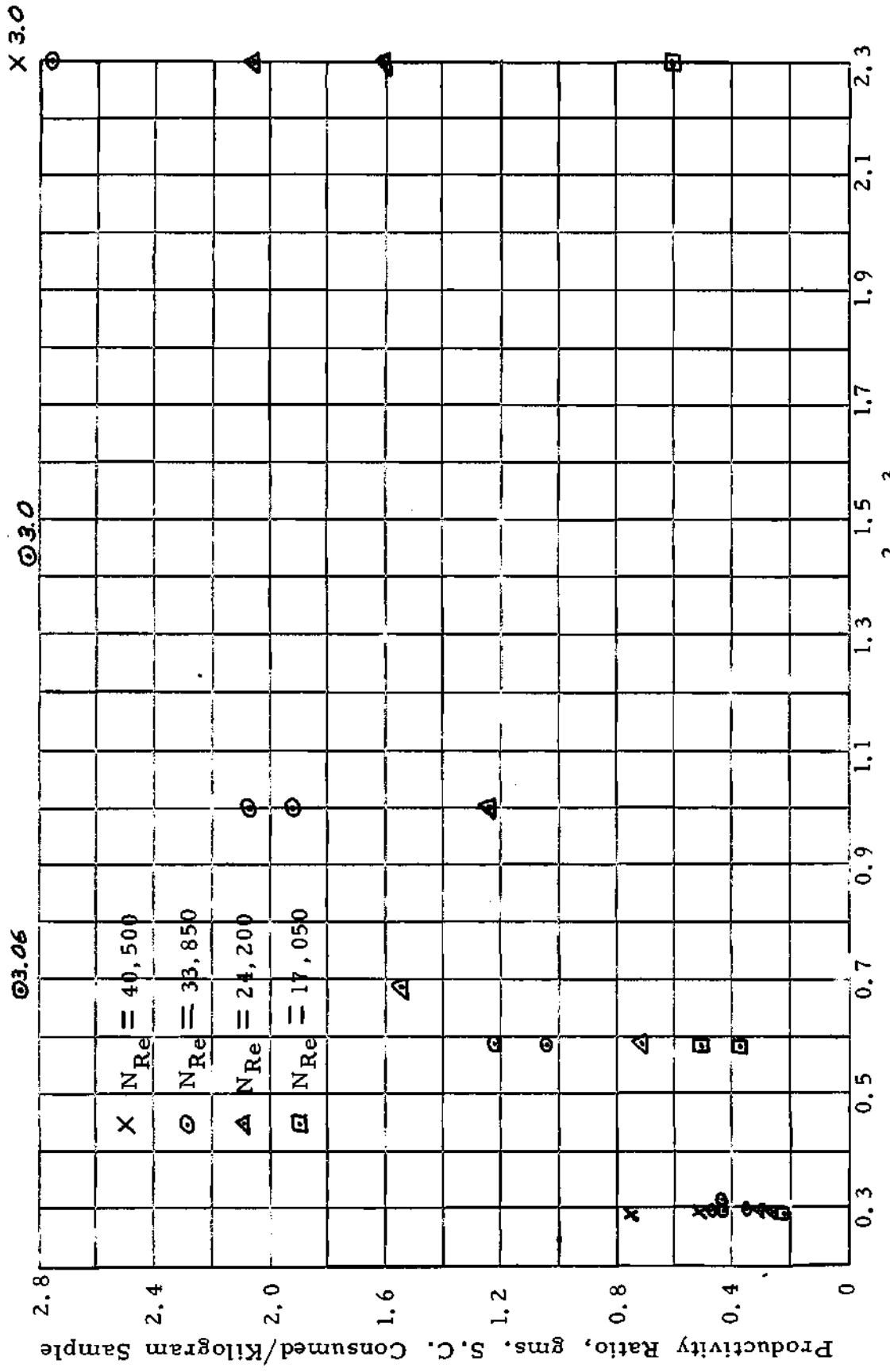


Figure 8. Productivity Ratio vs. (Sebacoyl Chloride)(HMDA)^2 for 8.5 inch Reactor

productivity ratio indicates the production of polymer that can be obtained from a particular tubular reactor for a given thruput at specified process conditions. Productivity ratio is not a rate as reaction time does not influence it. It will be seen later that reactor residence time has little effect on productivity ratio in most cases.

Figure 3 illustrates productivity ratio for the $36\frac{1}{2}$ inch reactor as a function of Reynolds number and the product of reactant concentrations, each raised to the first power. Figure 4 shows the same data plotted as a function of Reynolds number and the product of sebacoyl chloride concentration raised to the 1.3 power and HMDA concentration to the first power. Figure 5 illustrates productivity ratio for the $8\frac{1}{2}$ inch reactor as a function of Reynolds number and the product of the first powers of the two reactant concentrations. Figure 6 is identical to Figure 5 except that the sebacoyl chloride concentration is raised to the 1.3 power. Figure 7 is identical to Figure 5 except that the sebacoyl chloride concentration is squared, and Figure 8 is identical to Figure 5 except that the HMDA concentration is squared.

It is seen from these figures that productivity ratio definitely is not proportional to the second power (and, by inference, higher powers) of the concentration of either reactant. There is little difference between the correlation of productivity ratio with the first

and 1.3 powers of sebacoyl chloride concentration. However, the first power of sebacoyl chloride concentration correlates slightly better with productivity ratio at lower reaction rates; while the 1.3 power of sebacoyl chloride concentration correlates better at high reaction rates.

This apparent anomaly is believed to arise from the particular set of experimental conditions used in these runs. As an expedient for conserving carbon tetrachloride solvent and in permitting use of an available rotameter, an equal weight basis, instead of an equal volume basis, was chosen for the flow rates of the two reactant streams. Since carbon tetrachloride has a specific gravity of 1.594 at 20°C., 61.5 volume per cent of the liquid in the reactor was aqueous phase and 38.5 volume per cent was organic phase. At low conversions, this makes no appreciable difference as the concentrations of the phases would not change much during the course of the reaction. However, at higher conversions an appreciable concentration change does occur during the course of the reaction, and the sebacoyl chloride concentration would change more than the HMDA concentration. At some of the higher productivity ratios, 30 - 40 per cent of the sebacoyl chloride originally present was reacted; therefore, its concentration would change by this much. Another factor that prevented the HMDA concentration from changing appreciably is that excess HMDA was used in most of the runs.

Therefore, since the sebacoyl chloride concentration usually changed more than the HMDA concentration during a run (especially at high conversions), it would appear that sebacoyl chloride concentration is more important than the HMDA concentration with regard to controlling productivity ratio and more weight should be assigned to it. It is expected, however, that productivity ratio at all levels would be proportional to the product of reactant concentrations raised to the first power if equal volumes and molarities of both reactants had been used, or under any circumstances, if the reaction could be stopped at a low yield level. It is regrettable that equal weights instead of equal volumes were chosen as the basis of reactant stream flow rates as it is feared that this may have adversely affected the quality of the data somewhat.

It is concluded, therefore, from the above reasoning that productivity ratio in a tubular reactor at turbulent flow conditions is directly proportional to the product of reactant concentrations.

It is seen from Figures 3 - 8 that productivity ratio is highly dependent on the Reynolds number in the reactor. This indicates that the reaction rate of interfacial polymerization is faster than mixing and that the reaction rate is limited by the speed that the reactants can be brought into contact with each other. Since the reactants remained in the reactor only a fraction of a second (see reaction rate calculation in Appendix A), it is doubtful whether there

was sufficient time for diffusion to play a prominent role in the reaction.

The data indicate that reactor length and consequently reaction time does not have a pronounced effect on the extent of the reaction. This is illustrated in Figure 9 which is a composite of the curves from Figures 3 - 6. At first glance, this appears to be contradictory, as intuitively one expects that longer reaction time at identical Reynolds numbers should yield higher conversions. It must be remembered, however, that a tough polymer film forms at the interface during polymerization and that the process must slow down appreciably when turbulence can no longer break apart this film and expose new surface. Of course, reactants continue to diffuse through the film and react, but this is a relatively slow process.

There is convincing evidence that film formation and not acid chloride hydrolysis or some other effect caused the reactions studied in this work to stop at relatively low conversions ($<$ 50 per cent). At reactant concentrations similar to those used in this work, Morgan (4) reported a yield of 90 per cent when sebacoyl chloride in carbon tetrachloride was reacted with hexamethylene diamine in water for 2 - 3 minutes in a Waring blender. If acid chloride hydrolysis were responsible for stopping the reaction, it would have done so under the conditions encountered in the blender. Tremendous

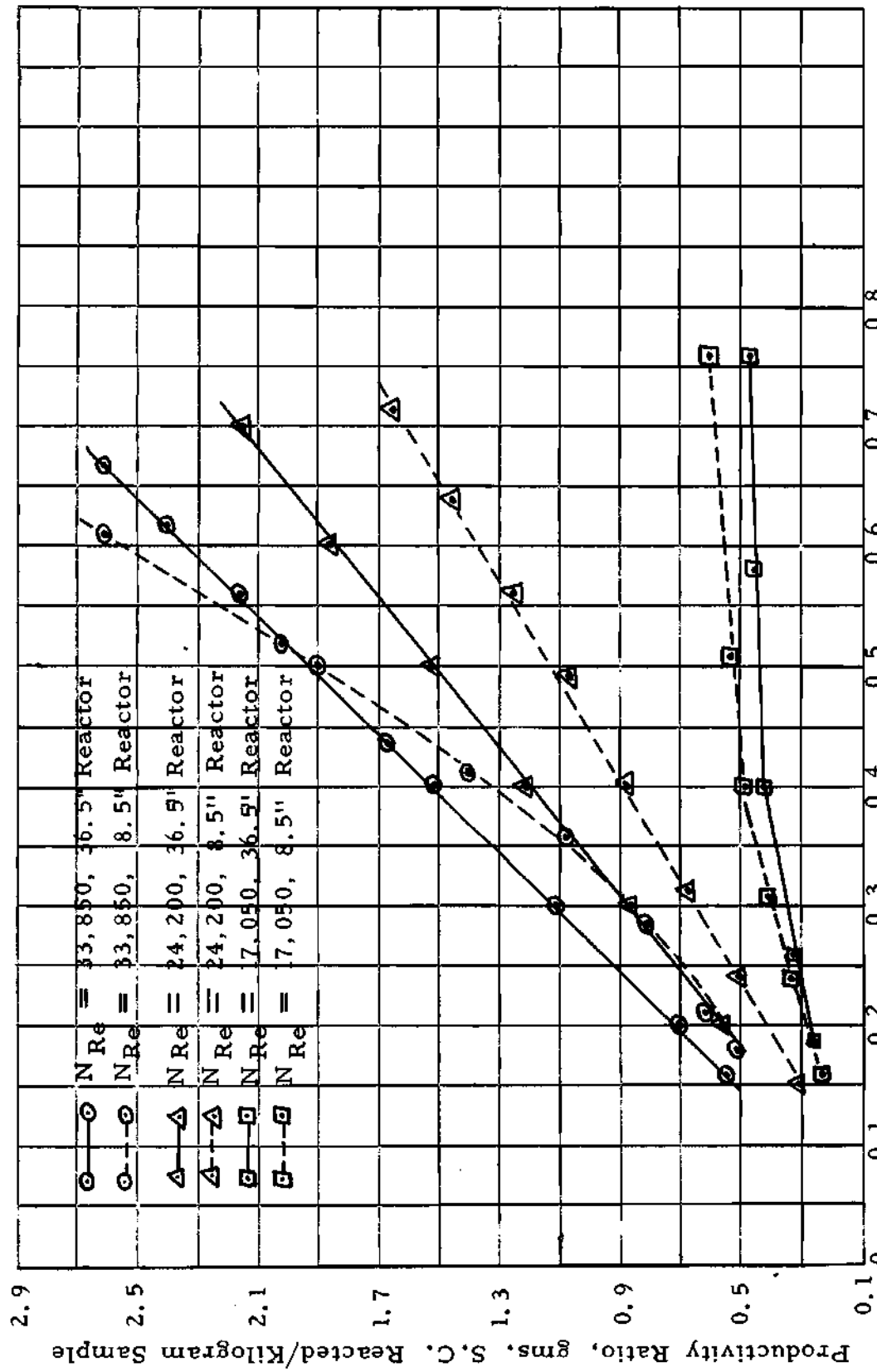


Figure 9. Comparison of Productivity Ratios of 8.5 inch and 36.5 inch Reactors

shear is generated in a Waring blender near the rotor blade, and it is speculated that this shearing force broke apart the polymer gel and allowed the reaction to proceed nearly to completion. No similar region of high shear exists in a tubular reactor; therefore, the reaction rate must decrease many fold when the film has built up to an extent where turbulence can no longer disrupt it and expose new surface. It is seen from Figure 9 that some differences do exist between extent of reaction in the two reactors at identical Reynolds numbers with the longer reactor featuring a higher conversion. This is not borne out by the lower pair of curves, Reynolds number equals 17,050; however, these curves were drawn from just a few data points. The differences between the upper two curves, however, are not pronounced and are nonexistent at high productivity ratios at a Reynolds number of 33,850. It must be concluded, therefore, that the reaction rate slows down and sometimes essentially stops after a certain critical time in the reactor. Two of the factors affecting this critical time are degree of turbulence and reactant concentrations.

It was reported in the literature (1), (2) that dispersing agents usually increase reaction rate; therefore, two runs, 9a and 9b, were made with 0.50 per cent "Duponol ME" (Du Pont trademark for sodium lauryl sulfate) added to the aqueous phase. Productivity ratios and consequently conversions were obtained that were 300 -

400 per cent higher than those obtained with similar runs where a dispersing agent was not used. It is believed that the dispersing agent accomplished this by dispersing the organic phase into smaller droplets; therefore, a larger organic phase surface area was generated, and a smaller volume of organic phase was trapped when the protective polymer film formed around the droplet.

Two other runs, 8a and 8b, featured a modified mixing tee where the organic phase entered the reactor through a small tube which was inserted through the center of the tee. The aqueous phase entered the reactor by flowing in through the annular space around the center tube. Consequently, the velocities of both streams in the initial mixing region were much higher than normal. The Reynolds number in the interior of the reactor, however, was the same as for previous runs. The higher mixing velocities resulted in better dispersion of the organic phase and formation of smaller droplets. Productivity ratios and conversions for these two runs were 200 - 250 per cent higher than normal. The results of these four runs indicate that productivity ratio and conversion are increased when better dispersion of the organic phase is obtained, regardless of the means used to obtain it.

A reaction rate constant was calculated for run 4a (see Appendix A). This particular run was made in the $8\frac{1}{2}$ inch reactor at a Reynolds number of 33,850 and fairly high reactant concen-

trations. The reaction rate calculation was made assuming that the reaction was second order and that diffusion and mixing could be neglected. A reaction rate constant of 1.2×10^3 liters/mole-second was obtained. The absolute reaction rates of unhindered acid chlorides with primary amines have been estimated to be in the range of 10^2 - 10^4 liters/mole-second (2). Since the reaction rate for run 4a falls in the middle of this range, it was concluded that the assumptions made were valid.

It is virtually impossible to obtain accurate reaction rate constants for interfacial polycondensation reactions due to the difficulty in measuring such extremely short reaction times and due to the unsteady state nature of the reaction. In run 4a, for example, the reactants were in the reactor only 0.06 of a second. It must be realized, therefore, that rate constant data for this type of reaction are not very meaningful due to dependence of reaction rate on turbulence and degree of dispersion of the organic phase, retardation of reaction rate by film formation, and difficulty in measuring reaction time.

Per cent conversion of the reactant present in smaller amount was calculated for all the runs. The results are listed in Table 1, Appendix B; conversions ranged from 3 - 48 per cent. The highest conversion was obtained for run 9a where a dispersing agent, "Duponol ME", was added to the aqueous phase. As stated pre-

viously, it is believed that relatively low conversions were obtained due to lack of a high shear environment in the reactor.

The reproducibility of these runs leaves something to be desired; however, it is felt that the reproducibility is reasonable considering the number of operations involved and the difficulties associated with sampling. Twenty-three pairs of runs were made at identical process conditions. The productivity ratio differences obtained in these pairs of runs are listed in Table 2, Appendix B. It is seen in Table 2 that the average difference for the twenty-three runs was 16.7 per cent. This per cent difference was based on the smaller of the two productivity ratios; therefore, a smaller figure would have been obtained if the larger of the two or a median productivity ratio had been used as the base.

It is believed that the largest single experimental error was due to flow fluctuations during polymerization, as flow rate has a dramatic effect on productivity ratio. Additional experimental errors were incurred in makeup of solutions, sampling, processing of samples, etc.

CHAPTER V

CONCLUSIONS

The following conclusions are drawn from the results of this study of the reaction between sebacoyl chloride and hexamethylene diamine in a tubular reactor at atmospheric pressure and 68° F:

(1) The speed of this reaction is slowed down appreciably by the formation of a polymer film at the interface between the two liquid phases.

(2) Productivity ratio is a function of reactant concentrations and Reynolds number with productivity ratio increasing as Reynolds number and reactant concentrations increase.

(3) Productivity ratio was found to be independent of reactor length over the range of lengths, reactant concentrations, and Reynolds numbers studied.

(4) At process conditions where film formation does not occur, the rate of this reaction was found to be essentially the same as that for aliphatic acid chlorides and primary amines in homogeneous solution; this reaction rate is 10^2 - 10^4 liters/mole-second.

(5) Productivity ratio and yield are extremely sensitive to droplet size and degree of dispersion of the organic phase.

APPENDICES

APPENDIX A - CALCULATIONS

I. Reynolds number of two phase liquid mixtures:

$N_{Re} = DG/u$ where D = diameter of pipe, feet;
$G = VP$, lbs. mass/second - $ft.^2$; and u = lbs. mass/second - ft.

The diameter of standard 3/8 inch stainless steel tubing = 0.305 inches; therefore, $D = 0.305/12 = 2.54 \times 10^{-2}$ ft.

Area of tubing $= \pi D^2/4 = 3.14 \times (2.54 \times 10^{-2})^2/4 = 5.065 \times 10^{-4} ft.^2$

The viscosity of a two-phase mixture of immiscible liquids was estimated from the relationship proposed in Perry's Chemical Engineers' Handbook (10). $u_G = u_x^x \cdot u_y^y$ where x and y are volume fractions. Equal flow rates of both phases on a weight basis were used for all runs. Since the specific gravity of CCl_4 at 20°C is 1.594, the volume fraction of $H_2O = 1.594/2.594 = 0.615$; the volume fraction of CCl_4 must equal 1.000 - 0.615 = 0.385. The viscosity of H_2O at 20°C = 1.05 cps. $= 0.705 \times 10^{-3}$ lbs. $_{mass}$/ft.-seconds. The viscosity of CCl_4 at 20°C = 1.00 cps. $= 0.672 \times 10^{-3}$ lbs. $_{mass}$/ft.-seconds.

Therefore, $u_{mixture} = (1.05)^{0.615}(1.00)^{0.385} = 1.03$ cps. $=$ 0.693×10^{-3} lbs. $_{mass}$/ft.-seconds.

For runs where the flow rate of each phase was 7.05 pounds/minute, the total flow $=$ 14.10 pounds/minute.

Therefore, G $=$ 14.10 lbs./minute x minute/60 seconds x $1/0.5065 \times 10^{-3}$ ft.^{2} $= 0.465 \times 10^{3}$ lbs./second-ft.^{2}

and $N_{Re} = \dfrac{(2.54 \times 10^{-2}\text{ft.})(0.465 \times 10^{3}\text{lbs./second-ft.}^2)}{0.693 \times 10^{-3}\text{lbs./second-ft.}} = 17,050$

II. Productivity Ratio and per cent conversion:

One mole of sebacoyl chloride (M.W. $=$ 239.0) and one mole of HMDA (M.W. $=$ 116.2) react to produce one repeat unit of 610 Nylon (M.W. $=$ 282.4). Since one molecule of Nylon contains ca. 75 repeat units, the polymer end groups may be neglected without introducing an appreciable error. The weight of polymer (in grams) collected in a sample is multiplied by 1000/sample weight in grams to convert to grams of polymer per kilogram of sample. This in turn is multiplied by 239.0/282.4 $=$ 0.846 to convert to grams of sebacoyl chloride reacted per kilogram of sample. The molarity of the original sebacoyl chloride solution is multiplied by 239.0 (M.W. of sebacoyl chloride) to convert to grams of sebacoyl chloride per liter of solution. This is divided by 1.594 (specific gravity of CCl_4) to

obtain grams of sebacoyl chloride per kilogram of solution. Since the reactor effluent is 50 per cent by weight organic phase, the grams of sebacoyl chloride/kilogram of CCl_4 solution is divided by two to obtain grams of sebacoyl chloride originally present in a kilogram of reactor sample. Per cent conversion is calculated by dividing the grams of sebacoyl chloride reacted per kilogram of sample by the amount of sebacoyl chloride originally present and multiplying the quotient by 100.

Productivity ratio is defined as the grams of sebacoyl chloride reacted per kilogram of reactor sample. This figure is obtained from the first part of the per cent conversion calculation.

III. Reaction Rate Constant Calculation for run 4a:

Volume of $8\frac{1}{2}$ inch reactor $= 5.065 \times 10^{-4}$ ft.^{2} x 8.5 ft./12 x 28.32 liters/ft.^{3} $= 1.016 \times 10^{-2}$ liters.

The reactor flow rate $=$ 1.05 gals. CCl_4/minute plus 1.68 gals. H_2O/minute x 3.785 liters/gallon $=$ 10.33 liters/minute.

$$\text{Reaction time} = \text{volume/flow rate} = \frac{1.016 \times 10^{-2} \text{ liters}}{10.33 \frac{\text{liters}}{\text{minute}} \times \frac{\text{minute}}{60 \text{ seconds}}} =$$

0.059 seconds.

Equation 23 in the book Chemical Kinetics by Laidler (11) describes the reaction rate of a second order reaction. This

equation states that $dx/dt = k(a-x)(b-x)$. In our case let a = molarity of HMDA and b = molarity of sebacoyl chloride; x = moles per liter of sebacoyl chloride (or HMDA) reacted. The molarity of each reactant in the reactor is equal to the molarity of the reactant solution multiplied by the volume fraction of that solution in the reactor. Therefore, $a = 0.1518 \times 1.594/2.594 = 0.0932$ and $b = 0.1000 \times 1.000/2.594 = 0.0386$. x = moles per liter of sebacoyl chloride in reactor times the conversion for this particular run (per cent conversion for run 4a = 36.65); therefore, $x = (0.0386)(0.3665) = 0.0142$.

The specific rate constant is calculated from equation 33 in Chemical Kinetics (11), $k = \frac{1}{t(a-b)} \times \ln \frac{b(a-x)}{a(b-x)}$.

$a - b = 0.0932 - 0.0386 = 0.0546$

$a - x = 0.0932 - 0.0142 = 0.0790$

$b - x = 0.0386 - 0.0142 = 0.0244$

and $t = 0.059$ seconds

Therefore, $k = \frac{1}{(0.059 \text{ seconds})(0.0546 \frac{\text{moles}}{\text{liter}})} \times \ln \frac{(0.0386)(0.0790)}{(0.0932)(0.0244)}$

$= 1.2 \times 10^3$ liters/mole-second

Appendix B - Table 1. Data Summary

Run No.	Temp. of Reactants °F	Reactor Length, Inches	Molarity Sebacoyl Chloride Solution	Molarity HMDA Solution	Ratio HMDA/S.C. in Reactor
1a	68.0	36.50	0.0478	0.030	1.00
1b	68.0	36.50	0.0478	0.030	1.00
1c	68.0	36.50	0.0478	0.030	1.00
2a	68.0	36.50	0.100	0.0759	1.21
2b	68.0	8.50	0.100	0.0759	1.21
2c	68.0	36.50	0.100	0.0759	1.21
2d	68.0	8.50	0.100	0.0759	1.21
2e	68.0	8.50	0.100	0.0759	1.21
2f	68.0	36.50	0.100	0.0759	1.21
2g	68.0	8.50	0.100	0.0759	1.21
3a	68.0	36.50	0.100	0.1518	2.42
3b	68.0	36.50	0.100	0.1518	2.42
3c	68.0	8.50	0.100	0.1518	2.42
4a	68.0	8.50	0.100	0.1518	2.42
4b	68.0	8.50	0.100	0.1518	2.42
4c	68.0	8.50	0.100	0.1518	2.42
4d	68.0	36.50	0.100	0.1518	2.42
4e	68.0	36.50	0.100	0.1518	2.42
4f	68.0	8.50	0.100	0.1518	2.42
5a	68.0	8.50	0.100	0.0759	1.21
6a	68.0	36.50	0.050	0.0759	2.42
6b	68.0	36.50	0.050	0.0759	2.42
6c	68.0	8.50	0.050	0.0759	2.42
6d	68.0	8.50	0.050	0.0759	2.42
6e	68.0	8.50	0.050	0.0759	2.42
6f	68.0	37.25	0.050	0.0759	2.42
7a	68.0	9.13	0.050	0.0759	2.42
7b	68.0	9.13	0.050	0.0759	2.42
7c	68.0	9.13	0.050	0.0759	2.42
7d	68.0	37.25	0.050	0.0759	2.42
7e	68.0	37.25	0.050	0.0759	2.42
7f	68.0	37.25	0.050	0.0759	2.42
7g	68.0	37.25	0.050	0.0759	2.42

Table 1. Data Summary (Continued)

Run No.	CCl_4 Phase Flow Rate lbs./min.	H_2O Phase Flow Rate lbs./min.	Reynolds Number	Productivity Ratio, gms. S.C. Consumed per Kilogram of Sample	Conversion per cent
1a	7.05	7.05	17,050	0.113	3.15
1b	7.05	7.05	17,050	0.099	2.76
1c	14.00	14.00	33,850	0.263	7.15
2a	7.05	7.05	17,050	0.454	6.05
2b	7.05	7.05	17,050	0.512	6.82
2c	14.00	14.00	33,850	1.201	16.01
2d	14.00	14.00	33,850	1.223	16.30
2e	14.00	14.00	33,850	1,040	13.87
2f	7.05	7.05	17,050	0.360	4.80
2g	7.05	7.05	17,050	0.371	4.95
3a	7.05	7.05	17,050	0.459	6.11
3b	14.00	14.00	33,850	2.562	34.18
3c	7.05	7.05	17,050	0.591	7.89
4a	14.00	14.00	33,850	2.745	36.65
4b	10.00	10.00	24,200	2.059	27.45
4c	10.00	10.00	24,200	1.598	20.70
4d	10.00	10.00	24,200	2.650	35.40
4e	16.40	16.40	40,500	3.035	40.45
4f	16.40	16.40	40,500	2.988	39.80
5a	10.00	10.00	24,200	0.723	9.60
6a	14.00	14.00	33,850	0.515	13.76
6b	14.00	14.00	33,850	0.544	14.41
6c	14.00	14.00	33,850	0.467	12.48
6d	14.00	14.00	33,850	0.443	11.85
6e	10.00	10.00	24,200	0.313	8.37
6f	10.00	10.00	24,200	0.398	10.62
7a	10.00	10.00	24,200	0.276	7.35
7b	10.00	10.00	24,200	0.346	9.25
7c	14.00	14.00	33,850	0.437	11.62
7d	14.00	14.00	33,850	0.531	14.17
7e	14.00	14.00	33,850	0.610	16.29

Table 1. Data Summary (Continued)

Run No.	Temp. of Reactants °F	Reactor Length, Inches	Molarity Sebacoyl Chloride Solution	Molarity HMDA Solution	Ratio HMDA/S.C. in Reactor
7h	68.0	9.13	0.050	0.0759	2.42
7i	68.0	9.13	0.050	0.0759	2.42
7j	68.0	9.13	0.050	0.0759	2.42
8a	68.0	35.25	0.050	0.0759	2.42
8b	68.0	35.25	0.050	0.0759	2.42
8c	68.0	7.13	0.050	0.0759	2.42
9a	68.0	37.25	0.050	0.0759	2.42
9b	68.0	9.13	0.050	0.0759	2.42
10a	68.0	37.25	0.050	0.1254	4.00
10b	68.0	37.25	0.050	0.1254	4.00
11a	68.0	37.25	0.090	0.1254	2.22
11b	68.0	37.25	0.090	0.1254	2.22
11c	68.0	9.13	0.090	0.1254	2.22
12a	68.0	37.25	0.1913	0.0600	0.50
12b	68.0	9.13	0.1913	0.0600	0.50
12c	68.0	37.25	0.1913	0.0600	0.50
12d	68.0	9.13	0.1913	0.0600	0.50
13a	68.0	9.13	0.1000	0.1000	1.59
13b	68.0	9.13	0.100	0.1000	1.59
13c	68.0	37.25	0.100	0.1000	1.59
13d	68.0	37.25	0.100	0.1000	1.59
13e	68.0	9.13	0.100	0.1000	1.59

Note: Acid Injection into Reactor started at Run 6f. Modified Mixing Tee used for Runs 8a, 8b, and 8c. 0.50 per cent "Duponol" added to Aqueous Phase for Runs 9a and 9b.

Table 1. Data Summary (Continued)

Run No.	CCl_4 Phase Flow Rate lbs./min.	H_2O Phase Flow Rate lbs./min.	Reynolds Number	Productivity Ratio, gms. S.C. Consumed per Kilogram of Sample	Conversion per cent
7f	16.40	16.40	40,500	0.646	17.24
7g	16.40	16.40	40,500	0.591	15.77
7h	16.40	16.40	40,500	0.520	13.88
7i	16.40	16.40	40,500	0.760	20.30
7j	7.05	7.05	17,050	0.228	6.08
8a	10.00	10.00	24,200	1.250	33.33
8b	10.00	10.00	24,200	1.163	31.00
8c	10.00	10.00	24,200	0.740	17.51
9a	14.00	14.00	33,850	1.799	47.90
9b	14.00	14.00	33,850	1.435	38.25
10a	14.00	14.00	33,850	1.098	29.25
10b	14.00	14.00	33,850	1.312	34.65
11a	14.00	14.00	33,850	2.460	36.25
11b	10.00	10.00	24,200	1.860	27.60
11c	14.00	14.00	33,850	2.979	43.95
12a	14.00	14.00	33,850	2.680	36.95
12b	14.00	14.00	33,850	3.060	42.65
12c	10.00	10.00	24.200	1.872	26.10
12d	10.00	10.00	24,200	1.541	21.45
13a	10.00	10.00	24,200	1.238	16.50
13b	14.00	14.00	33,850	2.081	27.80
13c	10.00	10.00	24,200	1.372	18.30
13d	14.00	14.00	33,850	2.023	27.00
13e	14.00	14.00	33,850	1.920	25.60

Appendix B - Table 2. Reproducibility of Runs

Run No.	Productivity Ratio	Run No.	Productivity Ratio	Absolute Difference	Per cent Difference
1a	0.113	1b	0.099	0.014	14.1
2d	1.223	2e	1.040	0.183	17.6
2a	0.454	2f	0.360	0.094	26.1
2b	0.512	2g	0.371	0.141	38.0
4b	2.059	4c	1.598	0.461	28.8
6a	0.515	6b	0.544	0.029	5.6
6c	0.467	6d	0.443	0.024	5.4
6e	0.313	7a	0.276	0.037	13.4
6c	0.467	7b	0.346	0.121	35.0
6d	0.443	7b	0.346	0.097	28.1
7b	0.346	7c	0.437	0.071	20.5
6c	0.467	7c	0.437	0.030	6.9
6d	0.443	7c	0.437	0.006	1.4
6a	0.515	7d	0.531	0.016	3.1
6b	0.544	7d	0.531	0.013	2.4
6a	0.515	7e	0.610	0.095	18.4
6b	0.544	7e	0.610	0.066	12.2
7d	0.531	7e	0.610	0.079	14.9
7f	0.646	7g	0.591	0.055	9.3
7h	0.520	7i	0.760	0.240	46.1
8a	1.250	8b	1.163	0.087	7.5
10a	1.098	10b	1.312	0.214	19.5
13b	2.081	13e	1.920	0.161	8.4
				$\Sigma =$	383.5

Note: Average per cent Difference = 383.5/23 = 16.7. Per cent Difference is calculated as absolute difference divided by the smaller of the two productivity ratios.

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